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## Gas separation using sol–gel derived microporous zirconia membranes with high hydrothermal stability<sup>☆</sup>

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## ABSTRACT

A microporous zirconia membrane with hydrogen permeance about  $5 \times 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ ,  $\text{H}_2/\text{CO}_2$  permselectivity of *ca.* 14, and excellent hydrothermal stability under steam pressure of 100 kPa was fabricated via polymeric sol–gel process. The effect of calcination temperature on single gas permeance of sol–gel derived zirconia membranes was investigated. Zirconia membranes calcined at 350 °C and 400 °C showed similar single gas permeance, with permselectivities of hydrogen towards other gases, such as oxygen, nitrogen, methane, and sulfur hexafluoride, around Knudsen values. A much lower  $\text{CO}_2$  permeance ( $3.7 \times 10^{-9} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ ) was observed due to the interaction between  $\text{CO}_2$  molecules and pore wall of membrane. Higher calcination temperature, 500 °C, led to the formation of mesoporous structure and, hence, the membrane lost its molecular sieving property towards hydrogen and carbon dioxide. The stability of zirconia membrane in the presence of hot steam was also investigated. Exposed to 100 kPa steam for 400 h, the membrane performance kept unchanged in comparison with freshly prepared one, with hydrogen and carbon dioxide permeances of  $4.7 \times 10^{-8}$  and  $\sim 3 \times 10^{-9} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ , respectively. Both  $\text{H}_2$  and  $\text{CO}_2$  permeances of the zirconia membrane decreased with exposure time to 100 kPa steam. With a total exposure time of 1250 h, the membrane presented hydrogen permeance of  $2.4 \times 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$  and  $\text{H}_2/\text{CO}_2$  permselectivity of 28, indicating that the membrane retains its microporous structure.

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## 1. Introduction

Due to their thermal, mechanical, and chemical stability [1,2], porous ceramic membranes are the most suitable membrane materials for implementation in many petro-chemical industrial processes where harsh environment, such as high temperature and high pressure, is often encountered. Microporous ceramic membrane-based gas separation offers an environment-friendly alternative to conventional separation technologies owing to its high energy efficiency and high performance (flux and selectivity) at elevated temperatures [1,3]. Because of its inherent microstructure [4], silica-based microporous membrane is one of the most promising molecular sieving materials in view of its excellent separation performance towards small gaseous molecules such as  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{CH}_4$ . This membrane has drawn a great deal of attentions for separation of industrial gas streams in comparison with organic

counterpart. However, it lacks microstructure stability in the presence of water at a temperature as low as 60 °C, restricting its industrial applications in gas separation such as steam-reforming of hydrocarbons and water-gas shift reaction [5]. Humidity can induce the densification of microporous silica network by the breakage of siloxane bonding in the presence of steam, followed by generation of silanol groups and subsequent recombination and rearrangement of them into the siloxane network [6]. Several approaches have been proposed for improving hydrothermal stability of silica membranes [7–9]. Firstly, metal or transition metal ions are chosen as dopants to modify the amorphous silica matrix. For example, Igi *et al.* [7] found that doping cobalt hampered the thermally induced molecular motion of silica matrix and, thereby, increased the hydrothermal stability of silica membrane. Secondly, organic functional groups were introduced into silica networks [10–13]. Duke *et al.* [11,12] reported an improved stability of carbonized silica membranes due to the remained carbon in the silica matrix, which reduces free motion of silanol groups. De Vos *et al.* [13] and Wei *et al.* [10] also dispersed organic functional groups into the silica matrix so as to make membrane structures more hydrophobic. Another strategy to overcome the instability of silica membrane in the presence of steam is to substitute tetraethylorthosilicate with other precursors, which are more hydrothermally stable, such as transition-metal alkoxides or bridged bis-silyl precursors. For example, Kanazashi *et al.* [14] fabricated a hybrid silica membrane by using 1,2-bis(triethoxysilyl)ethane

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(BTESE) as a precursor, with the membrane remaining stable in 3 kPa steam for 90 h. Nevertheless, imparting excellent hydrothermal stability to microporous membranes while retaining their flux and selectivity properties remains one of the challenges in membrane research field.

Other oxide materials such as titania, zirconia and Ti/Zr composite membranes are considered more stable in the presence of hot steam and promising for gas separation [5]. However, their permselectivities to gases with relatively small kinetic diameters, such as H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub>, are generally in the range of Knudsen values. For example, Shibao *et al.* [15] and Gu *et al.* [16] fabricated zirconia-based gas separation membranes, with permeance to H<sub>2</sub> as high as  $5 \times 10^{-6} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$  at the expense of low permselectivity (5–6) to H<sub>2</sub>/CO<sub>2</sub>, which is slightly higher than the Knudsen value (4.7). Coterillo *et al.* [17] reported a much lower ideal separation factor (<3) of He/CO<sub>2</sub> for a tubular ZrO<sub>2</sub> membrane calcined at 400 °C. Kreiter *et al.* [18] obtained similar results with titania microporous membranes. One of the main obstacles in such investigations is that either mesoporous membranes (with pore size larger than 2 nm) or nearly dense structures are obtained for the fabrication of titania, zirconia or Ti/Zr composite gas separation membranes. It is very difficult to quantitatively tune the pore size of oxide-based membranes in the range of 0.3–0.5 nm, which is suitable for the separation of gases with relatively small sizes, such as hydrogen and carbon dioxide.

Inspired by the results in our previous study [19], in view of zirconia as a common catalyst with acidic properties [18,20], our motivation in this research is to tune the pore size and surface acidity of zirconia membrane for the separation of H<sub>2</sub>/CO<sub>2</sub> under hydrothermal condition. In this study, we report the single gas permeance of microporous zirconia membranes and examine the hydrothermal stability of a sol–gel derived microporous zirconia membrane in the presence of 100 kPa steam.

## 2. Experimental

### 2.1. Sol synthesis

Zirconia polymeric sol was synthesized by using zirconium *n*-propoxide (70% in propanol, ABCR GmbH, denoted as ZnP) as a precursor and diethanolamine (DEA) as a chelating agent. 4.5 ml of ZnP was added to 20 ml of 1-propanol, and then 2.1 ml of DEA was drop-wise introduced into the ZnP solution with vigorous stirring. Both operations were carried out in a nitrogen glove box. The mixture was immediately placed in an ice bath to prevent premature hydrolysis. 0.9 ml of deionized water was drop-wise added into the above-mentioned solution with vigorous stirring and subsequently maintained at 273 K for hydrolysis and condensation for 12 min. The obtained zirconia polymeric sol had a final molar ratio of 1:28.9:2.2:5 (ZnP:1-propanol:DEA:H<sub>2</sub>O) and was diluted 6 times with 1-propanol before dip-coating.

### 2.2. Preparation of powder and membrane

Supported microporous zirconia membranes were fabricated through a single dip-coating of zirconia sol onto home-made disk  $\alpha$ -alumina supported mesoporous  $\gamma$ -alumina layers under clean room (class 1000) conditions. The gamma alumina layer was calcined at 550 °C with the final pore size of 4–5 nm. Dip-coating was performed at a velocity of  $12 \text{ mm} \cdot \text{s}^{-1}$  by using a MEMDIP 5 coating device (Pervatech B. V., The Netherlands). Then zirconia membranes were calcined in the air at 350 °C, 400 °C and 500 °C for 3 h (referred to as Zr-350, Zr-400, and Zr-500, respectively), with both heating and cooling rates of  $0.5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ . Zirconia powder was obtained by drying corresponding zirconia polymeric sols in a Petri dish at 100 °C, followed by calcination procedure the same as that for supported zirconia membranes.

### 2.3. Characterization

Effective particle size in the zirconia polymeric sol was measured by using a Zetatrac analyzer (Microtrac Inc.), based on the dynamic light scattering and Mie scattering theory. The particle size distribution of polymeric zirconia sols was derived from a cumulant analysis in the Microtrac software. Thermal evolution of dried zirconia powder was determined using a combined thermogravimetry and differential thermal analysis (TG-DTA) apparatus (STA-449-F3, Netzsch), under air atmosphere (flow rate:  $30 \text{ ml} \cdot \text{min}^{-1}$ ) with a heating rate of  $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$  in the temperature range of 40–1000 °C. Phase composition of zirconia powder heat-treated at different temperatures and with steam treatment was evaluated by employing X-ray diffraction (XRD, Bruker D8, Advance diffractometer), using a target of Cu K $\alpha$  operated at 40 kV and 40 mA. Nitrogen adsorption measurements were conducted at 77 K (N<sub>2</sub>) on Belsorp-mini instrument (Bel Inc.). Prior to measurements, all samples were degassed at 200 °C for 3 h under vacuum. Temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD, TP5080, Xianquan Co. Ltd., Tianjin, China) was used to evaluate the acidity of zirconia powder before and after steam treatment.

Single gas permeation measurements of zirconia membranes were conducted in a dead-end mode set-up. The membranes were sealed in a stainless steel module using fluoroelastomer O-rings with the separation layer exposed to the feed side. The pressure difference across the membrane and the cell temperature were set at 0.3 MPa and 200 °C, respectively, while the permeate side was vented to the atmosphere. Single gas permeances of zirconia membranes were measured in sequence, starting with the smallest kinetic diameter, from H<sub>2</sub> (0.289 nm), CO<sub>2</sub> (0.33 nm), O<sub>2</sub> (0.346 nm), N<sub>2</sub> (0.365 nm), CH<sub>4</sub> (0.382 nm) to SF<sub>6</sub> (0.55 nm). The permselectivity, also known as ideal selectivity, was calculated based on ratios between permeance values for pure gases throughout the study. Hydrothermal stability of a membrane was tested by measuring its single gas permeance at 200 °C, before and after in-situ exposure to steam at 100 kPa over a total period of 1250 h. The temperature for exposure of membrane to steam was 200 °C. Further stability tests were carried out by putting zirconia powder in saturated steam at 200 °C (corresponding to a pressure of 1550 kPa) in an autoclave for 100 and 300 h. Nitrogen adsorption measurements, XRD and NH<sub>3</sub>-TPD characterizations were conducted on samples and compared with that of zirconia powder without steam treatment, so as to evaluate their hydrothermal stability.

## 3. Results and Discussion

### 3.1. Properties of zirconia polymeric sols

Fig. 1 shows the particle size distributions of zirconia polymeric sols immediately after synthesis and stored at  $-20 \text{ }^\circ\text{C}$  for various time intervals. The particle size of freshly prepared zirconia sol was in the range of 1.5–15 nm, with an average value of 3.3 nm. When stored at  $-20 \text{ }^\circ\text{C}$  for 1 month and 2 months, the particle size distribution shifted slightly, with the average particle size being 3.7 and 3.9 nm, respectively. With storage at  $-20 \text{ }^\circ\text{C}$  for over 3 months the particle size increased slightly to an average value of 4.6 nm. However, the maximum particle size did not vary much during the storage. The sol kept clear and transparent after storage at  $-20 \text{ }^\circ\text{C}$  over 3 months. The results confirm a high sol stability and suitable particle size distribution as required for practical deposition of the sol onto a mesoporous substrate.

### 3.2. Thermal evolution of sol–gel derived zirconia powder

Fig. 2 shows thermogravimetric (TG) and differential thermal analysis (DTA) data of dried zirconia powder. Four exothermic peaks are apparent, corresponding to temperatures 347.5 °C, 387.5 °C, 492.5 °C and 682.5 °C. The initial mass loss up to temperature of 250 °C is due to the removal of physically absorbed water and solvent. The exothermic

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